Standard Operating Procedure for the Analysis of Trihalomethanes in Water by Purge and Trap Capillary Gas Chromatography/Mass Spectrometry

1.0 Scope and Application

1.1 This method is to be used for the identification and measurement of the four trihalomethane(THM's) disinfection by-products found in drinking water. This method is based on EPA Method 524.2. Analytes that can be measured using this procedure are listed below alphabetically along with the analyte number assigned to that compound in the Chemistry Division's Laboratory Information Management System(LIMS)

Analyte	Analyte Number
Bromodichloromethane	40710
Bromoform	40730
Chloroform	40700
Dibromochloromethane	40720

1.2 This SOP is applicable to analyte concentrations ranging from 0.5 ug/L to approximately 60 ug/L. Analyte detection limits vary by compound. Some compounds are detectable to much lower than 0.5 ug/L while others are borderline detectable at that level. The reporting level for this SOP is 0.5 ug/L and a standard of this concentration must be analyzed to verify each analyte's detectability at this level.

2.0 Summary of Method

2.1 The trihalomethanes(THM's), internal standard, and surrogates are purged from the water matrix by bubbling helium through the samples. Purged components are trapped in a tube containing a suitable sorbent material. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components through a transfer line into a capillary gas chromatography (GC) column interfaced to a mass spectrometer(MS). The column is temperature programmed to facilitate the separation of the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. Analytes are quantitated

versus standards that are purged in the same manner as the samples. The concentration of each analyte is determined by relating the MS response of the quantitation ion produced by that analyte to the MS response of the quantitation ion produced by the internal standard. Surrogate analytes, whose concentrations are know in every sample, are measured with the same internal standard calibration procedures.

3.0 Definitions

3.1 Internal standard(IS) - A pure analyte added to a sample, extract, or standard solution in a known amount and is used to measure the relative responses of method analytes and surrogates that are components of the sample or solution. The internal standard must not be a sample component.

3.2 Surrogate analytes(SU) - An analyte which is extremely unlikely to be found in any sample that is added to the sample in known amounts before extraction and is measured using the same procedures that are used to measure other analytes. The purpose of surrogates is to monitor method performance with each sample.

3.3 Laboratory reagent blank(LRB) - An aliquot of reagent water used to make standards and quality assurance samples that is taken and analyzed in the same manner as all standards and samples. The lab blank is used to determine if analytes or other interferences are present in the laboratory environment, reagents, or the apparatus.

3.4 Trip blank - Reagent water that is placed in a sample container in the laboratory and included in the shipment to the sample site so it is exposed to the same conditions that samples are. The purpose of the trip blank is to determine if analytes or other interferences are present in the field environment.

3.5 Laboratory fortified blank(LFB) - Reagent water to which known quantities of analytes are added in the laboratory. The source of analytes must be different than that used to prepare the standards. The LFB is analyzed exactly like a sample. It's purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.6 Reagent water - Laboratory purified water that is used to prepare all standard, quality control, and blank solutions.

3.7 Stock standard solution - A concentrated solution containing method analytes, usually purchased commercially.

3.8 Calibration standard - A solution prepared from the stock standard solution used to calibrate the instrument.

4.0 Interferences

4.1 Major contaminant sources are volatile materials in the laboratory, impurities in the helium purging gas, impurities in the sorbent trap, and impurities in the methanol used to prepare the internal standard and surrogate solution. The use of Teflon tubing, Teflon thread sealants, or flow controllers with rubber components should be avoided since these materials out-gas organic compounds which will be concentrated in the trap during the purge step. Analysis of laboratory blanks provides information about the presence of contaminants. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of THM's is analyzed immediately after a sample containing relatively high concentrations of THM's. Lab blanks should be analyzed after every sample to minimize sample cross-contamination.

4.3 Special precautions must be taken to reduce methylene chloride interference. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate Teflon tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4.4 Analytes can be present in the methanol used to prepare the internal standard and surrogates solution. The methanol should be evaluated before preparation of the spiking solution.

5.0 Safety

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined, therefore each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized.

5.2 The following analyte has been tentatively classified as a known or suspected human or mammalian carcinogen: Chloroform. Pure standard materials and stock

standard solutions of this compound should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of this toxic compound.

5.3 This method does not address all safety issues associated with its use. This laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS's) should be available to all personnel involved in this analysis.

6.0 Supplies and Instrumentation

6.1 Supplies

6.1.1 Sample containers - 40 mL amber glass vials equipped with open caps and Teflon faced silicone septa. Prior to use, vials and septa should be washed with detergent and rinsed with tap and distilled water. The vials should be allowed to dry at room temperature and then be placed in a 120 degree C oven for a minimum of 1 hour. Septa are not placed in the oven. Vials remain in the oven until they are ready to be used for sampling or for standard preparation.

6.1.2 Liquid nitrogen for cryo-cooling of the cryofocuser and the GC oven

6.1.3 Ultra-high purity helium to supply carrier gas for the GC and purge gas for the Tekmar 3100

6.1.4 Other supplies such as volumetric flasks and pipets are common laboratory equipment and will not be listed here.

6.2 Instrumentation - The required instrumentation to perform this analysis includes a purge and trap system and gas chromatograph(GC) equipped with a mass spectrometer(MS) and a data acquisition/processing system. The following sections will describe the systems that are in use in the laboratory as of this revision. Note: Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other that those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.2.1 Purge and trap system - The purge and trap system consists of a Tekmar

SOLATek 72 as the sampling system, a Tekmar 3100 as the purge and trap system, and a Tekmar cyrofocusing module to allow the introduction of the analytes to the column at sub-ambient temperatures.

6.2.1.1 The Tekmar SOLATek 72 acts as the sampling device to introduce the sample to the purge and trap system. The SOLATek 72 is capable of sampling 5, 10, 15, 20, or 25mL water. Sample filling and transfer is achieved by supplying the unit with adequate helium pressure. The SOLATek 72 also contains reservoirs for the internal standard and surrogates spiking solution. This can be added in 5, 10, 15, 20, or 25uL aliquots to the samples during the sample transfer to the purge and trap system.

6.2.1.2 The Tekmar 3100 is the purge and trap apparatus. The sample is transferred from the SOLATek 72 to a sparge tube on the Tekmar 3100. The sparge tube has a glass frit on the bottom so that the helium purge gas passes through the sample as finely divided bubbles. This increases surface area of the purge gas and improves the efficiency of the analyte extraction. The purge gas extracts the analytes and transfers them to the sorbent trap, a tube coated with sorbent material. This application uses Purge Trap K(Vocarb 3000) as the trap. The trap contains CarbopackB/Carboxen 1000 & 1001. Traps are purchased from Supelco (Catalog number 2-4920). The purge trap must be conditioned prior to sample analysis following the suppliers guidelines. When the purge stage is complete, the trap is heated rapidly to desorb(remove) the analytes from the trap. The analytes are transferred from the trap to the cyrofocusing unit at the GC through a heated transfer line (Tekmar number 14-0539-002).

6.2.1.3 The cryofocusing unit is situated on the Hewlett-Packard 5890 GC and allows for subambient cooling of the analytes. The cyrofocusing unit is cooled to -150 degrees by liquid nitrogen. The analytes arrive at the unit through the transfer line and are slowed significantly by the low temperature. This allows for a concentration of all analytes at the head of the column. The GC oven is at 0 degrees and is heated slowly to allow for separation of the early eluting analytes.

6.2.2 Gas Chromatography/Mass Spectrometer/Data Acquisition-Processing

The GC/MS and data system consist of a Hewlett-Packard 5890 GC, a Hewlett-Packard 5972 MS and Hewlett-Packard Chemstation Data Acquisition and processing software. The components will be discussed briefly here and in greater detail in Section 11.

6.2.2.1 The HP5890 GC is configured to allow sample introduction through the cryofocusing unit through a specialized injection port (not the standard A and B ports). The GC is temperature programmable and is able to provide a constant helium flow throughout the analysis. The column used for this application is:

30 m x 0.25 mm ID DB-5MS with a 0.5 um film thickness from J & W Scientific(Catalog # 122-5536)

6.2.2.2 The HP5972 MS is directly interfaced with the GC column by positioning the column end within a few mm of the ion source. The MS is programmed to scan from 35 to 300 amu.

6.2.2.3 The Chemstation software allows for data collection and processing. It runs in Windows environment and data can be collected and stored while in the background.

7.0 Reagents and Standards

7.1 Reagents

7.1.1 Ascorbic acid - ACS reagent grade, granular

7.1.2 Reagent water - Laboratory distilled water purified by a Barnstead II water purification system. This system is a series of 4 cartridges designed to remove ions and organic compounds from the water.

7.1.3 Hydrochloric acid - Trace analyzed grade

7.1.4 Methanol - HPLC grade or better

7.2 Stock Standard Solutions

7.2.1 Internal standard/surrogates stock solution - EPA 524.2 Fortification Solution purchased from Supelco (Catalog number 4-7358) and contains the compounds listed below at 2000 ug/mL in methanol:

Fluorobenzene - Internal standard
4-Bromofluorobenzene - Surrogate 1 (S1)
1,2 - Dichlorobenzene-d4 - Surrogate 2 (S2)

See section 7.3.1 for preparation of the spiking solution.

7.2.2 THM standard stock solution - Trihalomethanes Calibration Mix purchased from Supelco (Catalog number 4-8746) and contains all method analytes at 200 ug/mL in methanol.

See section 7.3.2 for preparation of the calibration standards from this stock solution.

7.2.3 LFB Stock solution - Trihalomethanes Calibration Mix purchased from Supelco (Catalog number 4-8746) and contains all method analytes at 200 ug/mL This stock solution must be a different stock solution than that which is used to prepare the calibration standards.

See section 7.3.3 for preparation of the LFB from this stock solution.

7.3 Preparation of Standard Solutions

7.3.1 Internal standard/surrogates solution - Dilute the Supelco stock solution (4-7358) in the appropriate reservoir on the SOLATek 72. The reservoir holds about 22 mL liquid. Dilute 100 uL to 22 mL methanol. Mix the contents well. Each sample is spiked by the SOLATek 72 with this solution.

7.3.2 Calibration solution preparation - Dilute the Supelco stock solution (4-8746) as indicated below. A 25 uL gas tight syringe is required. Ten calibration solutions are normally prepared ranging from 0.5 ug/L to 60 ug/L. The system is calibrated as high as 60 ug/L because samples will routinely have analyte levels in that range. The highest standard will require the addition of 2 aliquots from the stock vial. Rinse the 25 uL syringe five times with methanol. Then, using the syringe, puncture the cap on the vial of stock solution and withdraw and discard 25 uL of stock 2 times. Then rinse the syringe in the stock solution several times to remove any trapped bubbles. When bubbles are no longer present, withdraw the appropriate amount of stock and inject it immediately into the appropriate volume of water for dilution. Discard the punctured cap and replace with a new cap after all calibration solutions have been

prepared. Mix the contents by inverting the flask 3 times only. Excessive mixing may result in loss of analytes. Immediately transfer the calibration solutions to labelled, prepared THM vials. Cap and store the vials until ready for analysis.

Standard 1 = 0.5uL/200mL water
200 ug/mL X 0.0005mL/0.2L = 0.5 ug/L
Standard 2 = 1.0uL/200mL water
200 ug/mL X 0.001mL/0.2L = 1.0 ug/L
Standard 3 = 2.5uL/200mL water
200 ug/mL X 0.0025mL/0.2L = 2.5 ug/L
Standard 4 = 5.0uL/200mL water
200 ug/mL X 0.005mL/0.2L = 5.0 ug/L
Standard 5 = 5.0uL/100mL water
200 ug/mL X 0.005mL/0.1L = 10.0 ug/L
Standard 6 = 10.0uL/100mL water
200 ug/mL X 0.010mL/0.1L = 20.0 ug/L
Standard 7 = 15.0uL/100mL water
200 ug/mL X 0.015mL/0.1L = 30.0 ug/L
Standard 8 = 20.0uL/100mL water
200 ug/mL X 0.020mL/0.1L = 40.0 ug/L
Standard 9 = 25.0uL/100mL water
200 ug/mL X 0.025mL/0.1L = 50.0 ug/L
Standard 10 = 30.0uL/100mL water
200 ug/mL X 0.030mL/0.1L = 60.0 ug/L

7.3.3 Laboratory fortified blank(LFB) preparation - The LFB solutions are prepared from the LFB stock solution as described in Section 7.2.3. THM concentrations in samples can vary widely so two LFB's are prepared to ensure accuracy at the lower and upper end of the calibration curves. These solutions are prepared using the same 25uL syringe that was used to prepare the calibration standards and withdrawing through the septum, with rinsing, as described in Section 7.3.2. Preparation of the LFB's are as follows:

LFB at 5.0 ug/L = 5.0uL LFB stock/200mL water
200 ug/mL x 0.005mL/0.20L = 5 ug/L

LFB at 30.0 ug/L = 15.0uL LFB stock/100mL water
200 ug/mL x 0.015mL/0.10L = 30.0 ug/L

The solutions are transferred to labelled, prepared sample vials and stored until analysis.

8.0 Sample Collection, Preservation, Shipping, and Storage

8.1 Sample collection and preservation

8.1.1 Samples are collected in 40 mL amber vials with open screw caps and teflon coated septa. The septa are teflon coated on one side only and this side must be in contact with the water sample. For samples collected outside the laboratory, vials and trip blanks are prepared here and shipped to the sampling location.

8.1.2 Four vials are filled for each sample location. Each vial must contain about 80 mg ascorbic acid added prior to the addition of any water.

8.1.3 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (about 10 minutes). Adjust flow to a rate which will not fill the vial so quickly as to cause spilling. When the vial is about half full, carefully add 2 drops of concentrated hydrochloric acid by a dropper bottle or add the contents of the vials included in the shipping containers. The addition of the hydrochloric acid should adjust the pH to less than 2. Continue filling the vial to overflowing and then cap the vial with the Teflon coated side of the septum facing the sample. Mix the sample by inverting it back and forth for 1 minute.
Note: Do not add the hydrochloric acid to the vial containing ascorbic acid before the addition of the sample.

8.1.4 When sampling from an open body of water, partially fill a larger container such as a quart jar or beaker with water and fill the sample vials by pouring from the large container.

8.1.5 Duplicate trip blanks must be handled with each sample set of 4 vials. The trip blanks are prepared in the laboratory with the same preservation

and pH adjustment as samples and are to remain with the sample vials at all times.

8.2 Shipping and storage

8.2.1 The samples must be chilled to about 4 degrees C when collected and maintained at that temperature until analysis. Samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will arrive at the laboratory with ice remaining in the cooler.

8.2.2 Samples must be stored at 4 degrees C or lower until analysis. The storage area must be free of organic solvent vapors and direct or intense light.

8.2.3 Samples must be analyzed within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

9.0 Quality Control

9.1 Quality control requirements are the initial demonstration of laboratory capability followed by analyses of lab blanks, trip blanks, lab fortified blanks, quality control samples, and continuing calibration samples with each analysis. The analyst must maintain records to document the quality of the data generated.

9.1.1 The initial demonstration of capability is performed by analyzing five replicates of a lab fortified blank prepared at a concentration of 5.0 ug/L. (See Section 7.3.3) The source of the stock solution should be different than that used to prepare the calibration standards. These samples should be prepared identically to how field samples would be - ie - with the addition of ascorbic acid and hydrochloric acid. Analyze the samples as described in Section 11.

9.1.1.1 Determine the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, the mean accuracy (as mean percentage of true value) for each analyte and the precision (as relative standard deviation) of the measurements for each analyte.

9.1.1.2 For each analyte, the mean accuracy should be between 80 and 120%. The precision of the recovery(relative standard deviation)

should be less than 20%.

9.1.1.3 A minimum detection limit (MDL)for each analyte has not been determined for each analyte in this method. Each analyte is routinely detectable at 0.5 ug/L and are reported as less than that value if appropriate.

9.1.2 A laboratory blank is analyzed during each analysis to determine the interferences that are present in the reagent water used to prepare standards and quality control samples. Several blanks are actually injected during the course of an analysis but are present only to separate samples and reduce the potential for cross-contamination between samples. At the beginning of each analysis, two water blanks are analyzed. The first is to clear the system of any accumulated interferences and the second is considered to be the "blank" sample. Concentrations of analytes present
are calculated versus the calibration curves and documented along with the other QA/QC data. Subtraction of blank levels from samples is not done.

9.1.3 One of the trip blanks from each sample set is analyzed along with the samples. Analyte concentrations(if any) in the sample are determined and if there are any results above the reporting level(usually 0.5 ug/L) then the trip blank is evaluated for those analytes. The concentrations of the blank levels are documented along with the concentrations of the sample levels. The purpose of this is to determine if concentrations in the samples could be caused by exposure to analytes at any time during the sampling procedure. If no analytes are present in the sample, the blank is processed to determine surrogate recoveries to assess method and instrument performance.

9.1.4 Laboratory fortified blanks (LFB) are analyzed as part of each analysis and are prepared as described in Section 7.3.3. The LFBs are prepared at 2 concentrations to test the lower and upper end of the calibration curves. The measured concentrations of the analytes in the LFBs must be plus or minus 30% of the true values to be acceptable. If acceptable accuracy cannot be achieved the problem must be solved before additional samples can be reliably analyzed.

10.0 Calibration and Standardization

10.1 The calibration and standardization information can be found as part of Section 11.

11.0 Procedure

11.1 The analysis of the THM's is a multi-step procedure that includes tuning of the mass spectrometer(MS), preparing a method for the gas chromatograph(GC), preparing an analysis sequence using the Chemstation software, preparing and starting the Tekmar SOLATek 72 and Tekmar 3100, installation of the liquid nitrogen cooling gas, and the processing and reporting of the data when the analysis is complete.

11.1.1 Tuning of the MS - The first step in performing an analysis is to tune the MS. The MS is tuned to ensure that the mass to charge ratios are correctly assigned. This is accomplished by introducing a known compound into the MS with known MS parameters. If the mass to charge ratios do not match the known values, the MS will adjust to match them. This ensures uniformity for all MS's.

11.1.1.1 In Windows on the Chemstation workstation, open Program Manager.

11.1.1.2 Open GC/MS Instrument # 1

11.1.1.3 Open ENVTop # 1. At this point, the software opens the most recently used analysis and downloads that method to the HP5890 Gas Chromatograph (GC). Reset the GC's temperature to 200 degrees on the instrument's keypad until the analysis begins.

11.1.1.4 From the menu bar under View, open Manual Tune.

11.1.1.5 Under Tune in the menu bar select Max Sensitivity Autotune. This will start the autotune and this will take about 5 minutes to complete. A printed copy of the tune results will be generated when the tune is complete.

11.1.1.6 Evaluate the tune results. Verify that the peak at mass 69 is the base peak and that peaks at masses 219 and 502 have detectable responses. Compare the current tune to the previous tune to see if any parameters have had major

changes. If any are present, retune the MS and if the changes are still present investigate and correct the problem. The EMVolts should be monitored over the course of time. As the multiplier ages, the EMVolts will increase. When the value appraches 2500, the multiplier is nearing the end of it's usefullness.

11.1.1.7 Store the tune report with all other tune reports to monitor MS performance.

11.1.1.8 Under File in the menu bar, save the tune values as atune.u.

11.1.1.9 Under View in the menu bar, open Top. This will reload the current method, so reset the GC oven temperature to 200 degrees until the analysis begins.

11.1.2 When the tune step has been completed, the next step is to prepare and load a method and a sequence.

11.1.2.1 Method parameters have been established and need not be changed. The method name is updated each time an analysis is started so each analysis has it's own unique method name. This allows for multiple analyses to be stored and processed simultaneously. The method is saved as TH followed by the date the analysis was begun - for example- TH990712.

11.1.2.2 Method GC parameters are as follows:

Column: DB-5MS, 30M x 0.25mm ID with a film thickness of 5 microns (J & W Catalog number 122-5536)
Carrier gas: Ultra-high purity helium supplied by auxiliary Channel C; PSI at 12.

Detector B(interface) = 280 degrees C
GC oven temperature program:
Initial temperature = 0 degrees for 5 minutes
Increase temp at 6 degrees/minute to 70 degrees

Hold for 0 minutes
Increase temp at 15 degrees/minute to 145 degrees
Hold for 2.50 minutes
Increase temp at 30 degrees/minute to 265 degrees
Hold for 5.0 minutes

Total run time = 33.17 minutes

All other GC parameters are established and need not be changed.

11.1.2.3 MS Acquisition parameters:

Acquisition mode: Scan
Solvent delay: 0.00 min
EM Absolute: false
EM Offset: 0
Low mass: 35
High mass: 300
Threshold: 150
Sample #: 2 A/D Samples: 4

The remainder of the MS acquistion parameters such as the target and quantitation ions for each analyte will be listed in Section 18.

11.1.2.4 In the GC/MS Instrument # 1 window menu bar, go to File, Save. Save the method as described in 11.1.2.1

11.1.2.5 In the GC/MS Instrument # 1 MSTop window, open Sequence, Use Quick Sequence Generator. Supply the requested information to build the analysis sequence. Save the sequence as VC followed by the date the analysis is to begin - for example VC990712.

11.1.2.6 When preparing the sequence, analyze a set of calibration standards at the beginning and end of the analysis. Also analyze the LFB at the beginning and end of the sequence.

11.1.2.7 In the GC/MS Instrument # 1 MSTop window, open Sequence, Load and Run Sequence. In this window

indicate that the full method is to be run and add a date extension to the data file directory - for example- C:\HPCHEM\1\METHODS\TH990712\990712. The date extension makes file management easier when transferring data to permanent storage at a later time. Click on Run Sequence in this window. This loads the indicated sequence and associated method which will set the GC oven temperature to 0 degrees. Reset the oven temperature to 200 degrees.

11.1.2.8 Return to GC/MS Instrument # 1 window. It should indicate that the system is in the "pre-run" stage and should also have the sample name and file number indicated.

11.1.2.9 At this point, the data acquisition portion of the analysis is ready to begin.

11.1.3 Preparation of the SOLATek 72 and the Tekmar 3100

11.1.3.1 The SOLATek 72 functions as the autosampler for the purge and trap and the Tekmar 3100 functions as the purge apparatus. Both are programmed in the Tekmar software on the computer. Typical operating parameters are listed below.

Sample purge volume: 25 mL
Internal Standard Volume: 5 uL

SOLATek72 rinse water temp = 90 degrees C
SOLATek72 sample cup temp = 30 degrees C

SOLATek72 sample needle temp = 30 degrees C
SOLATek72 transfer line temp = 125 degrees C
SOLATek72 soil valve temp = 125 degrees C
SOLATek72 sample sweep time = 0.50 min
SOLATek72 needle rinse volume = 15 mL
SOLATek72 needle sweep time = 1.00 min
SOLATek72 bake rinse volume = 15mL
SOLATek72 bake sweep time = 1.00 min
SOLATek72 bake drain time = 1.00 min
SOLATek72 number of bake rinses = 1

Tekmar 3100 valve oven temp = 175 degrees C
Tekmar 3100 transfer line temp = 175 degrees C
Tekmar 3100 sample mount temp = 45 degrees C
Tekmar 3100 MCS temp = 35 degrees C
Tekmar 3100 MCS bake temp = 310 degrees C
Tekmar 3100 purge ready temp = 33 degrees C
Tekmar 3100 purge temp = 0 degrees C
Tekmar 3100 turbo cool temp = -20 degrees C
Tekmar 3100 GC start = end of desorb
Tekmar 3100 GC cycle time = 0.00 min
Tekmar 3100 sample heater = off
Tekmar 3100 sample temp = 40 degrees C
Tekmar 3100 sample preheat time = 0.00 min
Tekmar 3100 purge time = 10.00 min
Tekmar 3100 dry purge time = 3.00 min
Tekmar 3100 desorb preheat temp = 245 degrees C
Tekmar 3100 desorb time = 5.00
Tekmar 3100 desorb temp = 255 degrees C
Tekmar 3100 bake time = 15.00 min
Tekmar 3100 bake temp = 265 degrees C
Tekmar 3100 cryofocuser = On
Tekmar 3100 cryo standby temp = 150 degrees C
Tekmar 3100 cryo focus temp = -150 degrees C
Tekmar 3100 cryo inject time = 0.45 min
Tekmar 3100 cryo inject temp = 235 degrees C

11.1.3.2 Prepare a schedule on the SOLATek 72 program to analyze the samples. The analysis can be started as soon as enough samples are in place and can run while the rest of the

samples are being prepared.

11.1.4 Sample loading on the SOLATek 72 and beginning the analysis

11.1.4.1 Verify that sufficient internal standard/surrogates solution is in the reservoir on the SOLATek 72. If there is not enough to complete the analysis prepare new spiking solution as indicated in Sections 7.2.1 and 7.3.1.

11.1.4.2 Add the samples to the SOLATek 72.

11.1.4.3 Check the waste reservoir to be sure it has sufficient room for the volume of samples to be analyzed.

11.1.4.4 Begin the analysis by pressing the start button in the SOLATek 72 program. The liquid nitrogen cooling gas must be connected immediately if it has not been done prior.

11.1.5 Installation and application of the liquid nitrogen cooling gas

11.1.5.1 Liquid nitrogen is supplied in gas-paks, low pressure delivery devices. A union is provided at the top of the gas-pak for connection to the cryo-focusing unit at the top of the GC.

11.1.5.2 Connect the nitrogen supply and open the valve on the gas pak.

11.1.5.3 The GC oven temperature should be at 200 degrees C when the analysis is started on the SOLATek 72. When the purging of the first sample reaches the Dry Purge stage, the GC oven temperature must be set to zero degrees on the keypad of the GC. This is the only time this must be done.

11.1.6 Data processing - Injections may be processed as soon as they have completed. It is recommended that the first set of standards be processed as soon as possible so subsequent sample injections may be monitored for recoveries of surrogates and any unusual results that may require a sample to be reanalyzed. No results should be reported from this initial

calibration. When the second set of standards at the end of the run is complete, the final calibration curves can be prepared and the quality control and sample results can be calculated and reported versus these curves. The procedure for preparing calibration curves and determining results versus these is described in the following sections.

11.1.6.1 Preparation of calibration curves

11.1.6.1.1 The preparation of calibration curves begins by opening the GC/MS Instrument # 1 window in the Program Manager window.

11.1.6.1.2 Open the ENVDA # 1 window and under File in the menu bar load the appropriate method.

11.1.6.1.3 Under File in the menu bar load the file containing the 0.5 ug/L standard from the set of standards at the beginning of the analysis.

11.1.6.1.4 Under Quant in the menu bar, open Calculate/Generate report. A printed report is not necessary. The software will apply the method parameters to the data file and will generate a report to the monitor. Exit out of this report.

11.1.6.1.5 Under Quant in the menu bar open Qedit, Quant Results.

11.1.6.1.6 Under Qedit in the menu bar, go to CO Next compound. Repeat this procedure to page through all method analytes to verify that peaks are properly integrated. If a peak has been missed or not properly integrated, it can be manually integrated by clicking the right mouse button and dragging the baseline to both sides of the peak in the top window. Releasing the right mouse button will complete the integration and the area in

the lower right window should be updated. Continue this process until all analyte peaks are properly integrated. When all peaks are integrated satisfactorily, go to File in the menu bar and exit and save changes.

11.1.6.1.7 Under InitCal in the Menu bar, clear all calibration responses and clear all calibration levels. This is the only time that this must be done.

11.1.6.1.8 Under InitCal in the Menu Bar, go to Update levels. Indicate that a new level is being added, give it a unique 4 character level ID, and indicate the analyte and internal standard concentrations. Click on Do Update. This will add this calibration standard to the calibration curves.

11.1.6.1.9 Go to InitCal in the Menu Bar and open Edit Compounds. Change the surrogate concentrations to match the concentration of the internal standard.

11.1.6.1.10 Go to File in the Menu Bar and save the method.

11.1.6.1.11 Open the next calibration standard file and repeat the procedure described in steps 4 through 11. **Note:** Do not clear calibration levels and responses after the processing of the rest of the calibration standards. Repeat this process until all standards have been added to the calibration curves.

11.1.6.2 Processing samples versus the calibration curves.

11.1.6.2.1 In the ENVDA # 1 window menu bar, open File and load the file that contains the sample of interest.

11.1.6.2.2 Under Quant in the menu bar, select Calculate/Generate Report, Screen only and click on OK. This will calculate sample results versus the newly constructed calibration curves and generate a report to the monitor.

11.1.6.2.3 Exit out of the report in Multi-Vu as this is not the final report.

11.1.6.2.4 Under Quant in the menu bar open Edit Quant Results.

11.1.6.2.5 Under Qedit in the menu bar, go to CO Next compound. Repeat this procedure to page through all method analytes to verify that peaks are properly integrated. If a peak has been missed or not properly integrated, it can be manually integrated by clicking the right mouse button and dragging the baseline to both sides of the peak in the top window. Releasing the right mouse button will complete the integration and the area in the lower right window should be updated. Continue this process until all analyte peaks are properly integrated. When all peaks are integrated satisfactorily, go to File in the menu bar and exit and save changes.

11.1.6.2.6 In the menu bar under Quant, open Generate Report. **Note:** Do not open Calculate/Generate Report as this would recalculate the results and would undo the editing(if any) that was done in Step 5. Report may be sent to the screen and must be sent to a printer.

11.1.6.2.7 Load the next sample file to be processed and repeat the procedure described in steps 2 through 7. Continue reporting until all samples of interest have been processed.

11.1.7 Reporting of results

11.1.7.1 Several results must be recorded in whatever fashion is typical for the analyst and they are listed below:

Surrogate recoveries for each injection
Levels of analytes in the lab blank
LFB recoveries
Quality control sample results and recoveries
Continuing calibration sample results

11.1.7.2 The following results must be reported on the Laboratory Information Management System:

LFB recoveries
Sample results

12.0 Alternate Procedure - Non cryo cooling

An alternate GC procedure has been developed that does not require the use of liquid nitrogen for cryogenic cooling. This requires minor plumbing changes that will not be described in detail here. The most significant of the changes involves changing the carrier flow from auxiliary channel C to Auxilaury channel E which supplies carrier to inlet A on the GC. GC conditions and Tekmar conditions will detailed here. All other procedures are the same as in Section 11.

12.1 Typical GC Conditions

Column:	DB-624 (or equivlent), 25 meters x 0.2 mm ID, 1.12u film thickness. Column is connected to inlet A.
Inlet A temperature:	220 degrees C

Inlet A liner:	Glass, deactivated, direct, 2 mm ID, Agilent number 5181-8818
Temperature program:	40 degrees C for 4.0 min 6 degrees/min to 170 degrees C, hold for 0 min 20 degrees/min to 230 degrees hold for 5 min Run time = 33.67 min
Cryo:	Off
Inlet A	Constant flow; PSI = 8.5 at 40 degrees Auxiliary Pressure: Channel E, 45 psi
Inlet A purge:	Initial = On, Off at 1.25 min

12.2 Typical Tekmar Conditions

SOLATek72 rinse water temp = 90 degrees C
SOLATek72 sample cup temp = 30 degrees C
SOLATek72 sample needle temp = 30 degrees C
SOLATek72 transfer line temp = 125 degrees C
SOLATek72 soil valve temp = 125 degrees C
SOLATek72 sample sweep time = 0.50 min
SOLATek72 needle rinse volume = 15 mL
SOLATek72 needle sweep time = 1.00 min
SOLATek72 bake rinse volume = 15mL
SOLATek72 bake sweep time = 1.00 min
SOLATek72 bake drain time = 1.00 min
SOLATek72 number of bake rinses = 1

Tekmar 3100 valve oven temp = 125 degrees C
Tekmar 3100 transfer line temp = 125 degree C
Tekmar 3100 sample mount temp = 45 degrees C
Tekmar 3100 MCS temp = 35 degrees C
Tekmar 3100 MCS bake temp = 310 degrees C
Tekmar 3100 purge ready temp = 33 degrees C
Tekmar 3100 purge temp = 0 degrees C
Tekmar 3100 turbo cool temp = -20 degrees C
Tekmar 3100 GC start = start of desorb
Tekmar 3100 GC cycle time = 0.00 min
Tekmar 3100 sample heater = off
Tekmar 3100 sample temp = 40 degrees C
Tekmar 3100 sample preheat time = 0.00 min
Tekmar 3100 purge time = 11.00 min
Tekmar 3100 dry purge time = 2.00 min

Tekmar 3100 desorb preheat temp = 250 degrees C
Tekmar 3100 desorb time = 4.00
Tekmar 3100 desorb temp = 260 degrees C
Tekmar 3100 bake time = 15.00 min
Tekmar 3100 bake temp = 265 degrees C
Tekmar 3100 cryofocuser = Off

Sample Purge Volume: 25 mL
Internal Standard Volume: 5 uL

Refer to Section 11 for the rest of the procedural conditions.

13.0 Data Analysis, Calculations, and Reporting Results

13.1 The steps for performing data analysis, calculations, and reporting of results can be found in Sections 11.1.6 and 11.1.7.

14.0 Method Performance

14.1 The reporting level for all method analytes is 0.5 ug/L, which is the lowest concentration of calibration standard to be analyzed. This calibration level must be analyzed and shown to be detectable before 0.5 ug/L can be used as the reporting level.

14.2 Single operator precision and accuracy data are not available as of the revision of this method.

15.0 Pollution Prevention

15.1 No solvents are utilized in this method except the small volumes of methanol needed to make calibration standards. The only other chemicals used are the method analytes and they are present in small amounts that pose no threat to the environment.

16.0 Waste Management

16.1 There are no waste management issues involved with this method. Due to the nature of this method, the discarded samples are chemically less contaminated than when they were collected. Any excess samples or standards may be disposed of by flushing down a drain with tap water.

17.0 References

17.1 EPA Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.1, Edited by J. W. Munch(1995)

17.2 EPA Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.0, August 1992, from Methods for the Determination of Organic Compounds in Drinking Water Supplement II, EPA/600/R-92-129, August 1992.

17.3 Technical Notes on Drinking Water Methods, EPA-600/R-94-173, October 1994.

18.0 Tables, Diagrams, Flowcharts, Validation Data and Additional Information

```
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Operator   :
Acquired   : 10 Oct 2002   3:00 pm using AcqMethod TH021010
Instrument :
  HPMSD1
Sample Name: water - LRB
Misc Info  :
Vial Number: 5
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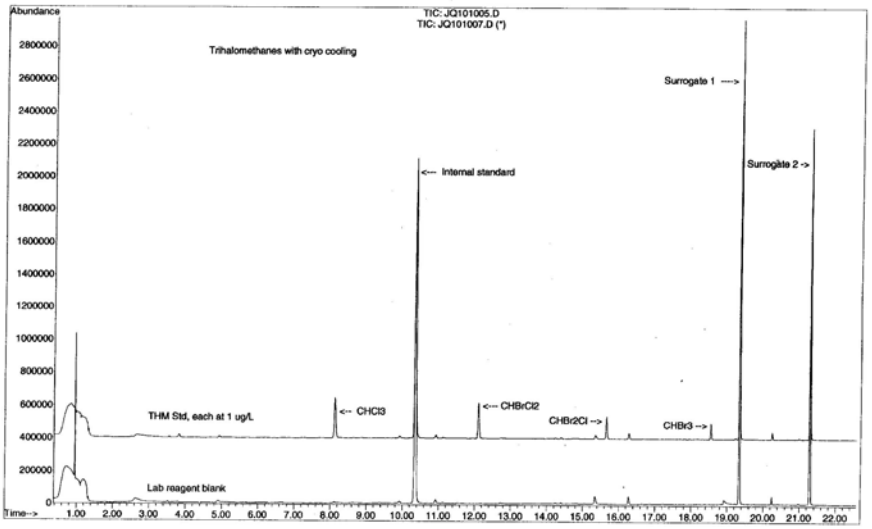


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Operator   :
Acquired   : 27 Mar 2003   1:01 pm using AcqMethod CF030327
Instrument :
  HPMSD1
Sample Name: water - LRB
Misc Info  :
Vial Number: 5
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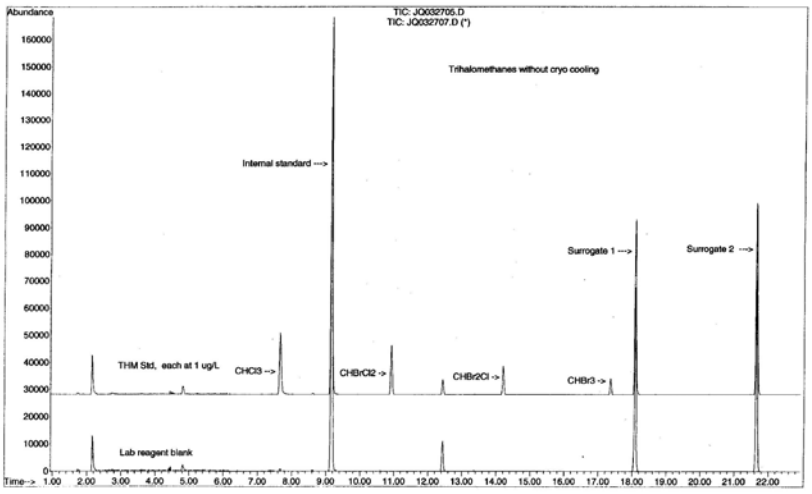

Table 1 Molecular Weight and Quantitation Ions for Method Analytes

Analyte	Molecular Weight	Primary Quantitation Ion	Secondary Quantitation Ions
Fluorobenzene (Int. Std.)	96	96.00	70.1, 75.1, 77.1
4-Bromofluorobenzene (Surrogate 1)	174	95.00	173.9, 175.9
1,2-Dichlorobenzene-d4(Surrogate 2)	150	152.00	115.0, 150.0
Bromodichloromethane	162	83.00	85.00, 126.85
Bromoform	250	172.80	174.80, 251.70
Chloroform	118	83.00	85.00
Dibromochloromethane	206	126.85	128.85